



TITLE:

Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by O₂ and BH₄-

AUTHOR(S):

Okamoto, Tadashi; Oka, Shinzaburo

CITATION:

Okamoto, Tadashi ...[et al]. Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by O₂ and BH₄-. Bulletin of the Institute for Chemical Research, Kyoto University 1986, 64(3): 104-106

ISSUE DATE:

1986-09-25

URL:

<http://hdl.handle.net/2433/77144>

RIGHT:

NOTE

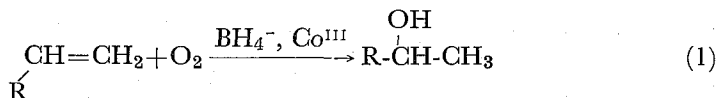
Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by O₂ and BH₄⁻

Tadashi OKAMOTO* and Shinzaburo OKA*

Received July 1, 1986

KEY WORDS: Oxygenation/ Olefin/ Secondary alcohol/ Cobalt complex/ Catalysis/

Oxygenation of aryl substituted olefins in the presence of cobalt(III) complex catalysts and BH₄⁻¹⁾ attracted attention as a unique hydration of olefins into alcohols under the basic reaction conditions²⁾ and also as a transition-metal catalyzed reaction of molecular oxygen under the reductive conditions relevant to oxygenases.³⁾



Although the reaction of aryl substituted olefins is not fast at room temperature and requires several days for completion, it is accepted as a synthetic method since the yield of product alcohol is generally high and the regioselectivity for benzyl alcohol-type product is quantitative. However, it was also reported that the reaction of 1-hexene, an aliphatic olefin, showed almost no regio-selectivity.¹⁾ To clarify the scope and limitation of this reaction, we examined several aliphatic olefins by the catalysis of bis(dimethylglyoximate)chloro(pyridine)cobalt(III), CoCl(DH)₂(py), as summerized in Table 1. The reactivity of cyclohexene was low compared with styrene by a factor of about 1/100, and steric crowding of substrate olefin further depressed the reactivity. A better result was obtained with meso-tetraphenylporphyrinatocobalt(II), CoTPP, as the catalyst instead of CoCl(CH₂py), but it was still insufficient for the synthetic purpose. Illumination by room fluorescent light had an acceleration effect on the oxygenation of cyclohexene, contrary to the results of aryl substituted olefins. With respect to the selectivity, differentiation between endo- and exo-double bonds was moderately attained in the reaction of 4-vinylcyclohexene. The double bond located on the side chain was preferred over the endocyclic double bond by a factor of 4/1 probably because of the steric reason. However, the regio-selectivity of the reaction, represented by the ratio of the yields of secondary alcohol over primary alcohol, which was 100/0 with aryl olefins, was disappointingly low showing virtually no selectivity with all aliphatic olefins examined except for 1-me-

* 岡本 忠, 岡信三郎: Laboratory of Organic Unit Reaction, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by O₂Table 1. Oxygenation of Aliphatic Olefins^{a)}

Olefin	Time	Yield of ROH ^{b)}	Selectivity
Cyclohexene	14 hr	16% (0.6)	—
4-Vinylcyclohexene	21 hr	12% (0.7)	endo/exo=1/4
4-Methylcyclohexene	21 hr	25% (1.1)	3-/4-Methylcyclohexanol=1/1
4-Methylcyclohexene ^{c)}	25 hr	85% (3.8)	3-/4-Methylcyclohexanol=1/1
1-Methylcyclohexene	12 day	40% (1.7)	1-/2-Methylcyclohexanol=7/93
1-Hexene	21 hr	16% (0.8)	1-/2-Hexanol=45/55
1-Hexene ^{d)}	12 hr	3300% (3.6)	1-/2-Hexanol=45/55
Isoprene	7 day	45% (5.3)	2-Methyl-3-butene-2-ol/ 2-Methyl-1-butene-3-ol=1/1

a) Olefin, 1 ml; catalyst, 150 mg; NaBH₄, 50 mg; dimethoxyethane, 5 ml, room temperature; dark.

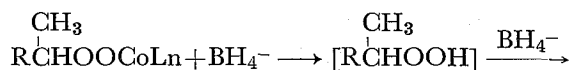
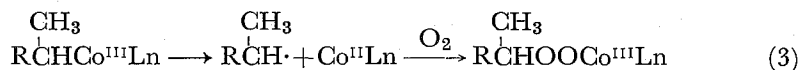
b) Yields based on the amount of catalyst. Values in the parenthesis show the yields based on the amount of substrate used.

c) Under room fluorescent light.

d) Catalyst (Co(TPP)), 6 mg; Et₄NBH₄, 145 mg, no solvent was used.

thylcyclohexene.

Now it can be concluded that the cobalt-catalyzed oxygenation of aliphatic olefins in the presence of BH₄⁻ is of little value in organic synthesis. However, the results are helpful for understanding of the reaction mechanism. Following are the major differences of aliphatic olefins in the oxygenation compared with aromatic olefins; 1) low reactivity, 2) low regioselectivity, and 3) acceleration by light. According to our previous proposal,¹⁾ the reactive intermediate of the present oxygenation is an organocobalt complex (Eqs 2-4).



The chemistry of organocobalt complexes is extensively examined nowadays,⁴⁾ and the bond dissociation energies were known for several carbon-cobalt bonds.⁵⁾ Thus the low reactivities of aliphatic olefins can be correlated with the high energy barriers for the cleavage of C-Co bonds of the intermediate organocobalt complexes. Acceleration with visible light is in line with the mechanism since such a light effect should be significant only for the dissociation of a rather strong C-Co bond. In fact, the C-Co bond of benzyl- or 1-phenylethylcobaloxime dissociated in the dark at room temperature, whereas methyl- or 2-phenylethylcobaloxime was stable under the same reaction conditions. The last complex dissociated in the light at room temperature. Similar discussion may hold for the low regioselectivity of aliphatic



Figure 1.

olefins. The difference of stabilization energies between radicals on C_α (A) and C_β (B) in Figure 1 (hence that of the corresponding energies of C-Co bonds) should be small for radicals generated from aliphatic olefins compared with those of aryl substituted olefins. If the regioselectivity is determined at the stage of the formation of C-Co bond, then the observed selectivity is the result of competition between the stability of the generated radical species and the steric interaction of the alkyl group with other ligands of the metal complex. The stabilization of radical A must exceed the steric repulsion for the aryl substituted olefins but not for aliphatic olefins.

EXPERIMENTAL

Catalysts were prepared according to the method in literature.⁶⁾ Experimental procedures of oxygenation were similar to those of the previous publication¹⁾ except that the reaction was carried out in dimethoxyethane rather than in dimethoxyethane-2-propanol.

REFERENCES

- (1) T. Okamoto and S. Oka, *J. Org. Chem.*, **49**, 1589 (1984).
- (2) CHEMTECH, 1985, 260.
- (3) M. Nozaki, *Top. Current. Chem.*, **78**, 145 (1979).
- (4) R. D. W. Kemmitt and D. R. Russell, "Comprehensive Organometallic Chemistry" ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Vol. 5, Pergamon Press, 1982.
- (5) J. Halpern, *Accounts Chem. Res.*, **15**, 238 (1984).
- (6) G. N. Schrauzer, "Inorganic Synthesis", **11**, 61 (1968).